TETRAKIS(TRIPHENYLSTANNYL)TIN¹

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As part of a study of the catenation and polymerization of Group IVB elements², it was desirable to investigate the properties of branched-chain polytin compounds. In 1923 Böeseken³ reported that a minor product from the reaction of phenylmagnesium bromide with stannous chloride (6:1 molar ratio) was a compound with the empirical formula, $(C_6H_5)_{12}Sn_5$. He could not distinguish among the three possible structures [(I), (II) and (III)] for this derivative, but he thought the tetrakis configuration (I) was the most likely structure. He reasoned that the latter structure

$$(C_{6}H_{3})_{3}Sn$$

$$(C_{6}H_{3})_{3}Sn-Sn(C_{6}H_{3})_{3} (C_{6}H_{3})_{3}Sn-[(C_{6}H_{3})_{2}Sn]_{3}-Sn(C_{6}H_{3})_{3}$$

$$(II)$$

$$(C_{1}H_{3})_{3}Sn$$

$$Sn(C_{6}H_{3})-Sn(C_{6}H_{3})_{2}-Sn(C_{6}H_{3})_{3}$$

$$(III)$$

$$(III)$$

$$(III)$$

should be the most stable of the three isomers, and, indeed, the compound which he isolated was one of the most thermally stable organotin compounds known, decomposing at 280°. One might also argue that the reaction conditions under which the compound was formed afford evidence for the tetrakis structure. If the pentatin had the straight chain structure (II), one might expect to find tritin or tetratin homologs in the reaction mixture. In contrast, the tetrakis structure is unique and could easily be formed in the absence of lower or higher homologs. In fact, the only two additional products obtained from the reaction were hexaphenylditin and tetraphenyltin.

Böeseken's compound is the only one in the literature which is assumed to contain a branched polytin chain. In view of the modification of properties which chain branching would be expected to cause in polytin compounds, an investigation of possible methods for preparing branched chain polytin compounds was undertaken. As an alternate synthetic method for tetrakis(triphenylstannyl)tin (I), the scheme below was carried out.

$$3 (C_{s}H_{s})_{3}SnLi + SnCl_{2} \longrightarrow [(C_{s}H_{s})_{3}Sn]_{3}SnLi \xrightarrow{(C_{s}H_{s})_{3}SnCl} (I)$$
(IV)

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It has been previously reported⁴ that the reaction of triphenylgermyllithium with germanium diiodide in a 3:1 molar ratio affords tris(triphenylgermyl)germane subsequent to hydrolysis. Presumably the intermediate in the reaction is tris(triphenylgermyl)germyllithium. By analogy, the reaction of triphenyltinlithium with stannous chloride would be expected to produce tris(triphenvlstannyl)tinlithium, (IV), which could be treated with triphenyltin chloride to form (I). When the reaction was run, there was obtained in 70 % yield, a compound which began to turn brown at approximately 280° and melted with tin deposition at 315-330°. A tin analysis and molecular weight determination (vapor pressure osmometer) indicated that the empirical formula was $(C_6H_5)_{12}Sn_5$. The infrared spectrum of the compound (in carbon disulfide) was indistinguishable from that of hexaphenylditin, showing only absorptions associated with the phenyl molety. The ultraviolet spectrum (λ_{max} in cyclohexane 275.5, 247 m μ) was distinctly different from that of hexaphenvlditin, which shows only a single maximum at 247.5 m μ^5 . The ultraviolet absorptions have been indicated to be characteristic of the Sn_5 skeleton⁶. The product could be recrystallized from benzene, chloroform or a carbon disulfide-acetone mixture without changing the melting point range. The solubility properties are in agreement with those for Böeseken's compound. It seemed likely that the two were the same; thus, Böeseken's preparation was repeated, and a compound melting at 315-330° decomp. was obtained in 2% yield (based on stannous chloride). The two compounds were shown to be identical by the superimposition of X-ray powder patterns.

The compound was prepared by two additional procedures, each of which started with a $(C_6H_5)_3$ Sn-containing compound. The X-ray powder patterns of the

$$4 (C_6H_5)_3 SnLi + SnCl_4 \longrightarrow (I) (9.7\%) + (C_6H_5)_4 Sn$$

$$+ (C_6H_5)_3SnCl + SLi + SnCl_4 \longrightarrow (1) (20.6\%) + (C_6H_5)_6Sn_2$$

compounds from the several syntheses were identical, and all showed the same ultraviolet spectrum. When phenyllithium was substituted for phenylmagnesium bromide in the reaction with stannous chloride, tetraphenyltin was the only product isolated.

Quite recently another study of compounds of the type, $[(C_6H_5)_3M]_4M$, has been reported⁷. Derivatives were prepared in which M corresponded to Pb and Sn, the latter product being obtained from triphenyltinlithium and stannic chloride as well as by Böeseken's method. A detailed structural examination of the tin compound has not, however, been reported, nor any of its chemistry investigated. A related tetrakis compound, tris(triphenylgermyl)(triphenylstannyl)silane, was prepared some time ago⁸, but was not investigated in any detail structurally or chemically.

The methods of preparation themselves offer strong evidence that the tin compound has the tetrakis configuration (I) and not the isomeric structures (II) and (III). Further, crystals from carbon disulfide-acetone were suitable for an X-ray single crystal study. This analysis has given the unit cell dimensions. From considerations of the pseudosymmetry observed and the packing of the molecules in the unit cell, it is concluded that the tetrakis structure is the most probable one.

Chemical evidence for the structure has likewise been obtained. The most significant result was afforded by reaction of the compound with four moles of iodine. Triphenvltin iodide was obtained along with a product which was thought to be

$$(I) \div \downarrow I_2 \longrightarrow \downarrow (C_6H_5)_3SnI \div SnI_4$$

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stannic iodide. There was no evidence for the formation of diphenyltin diiodide or phenyltin triiodide. Likewise, reaction with an excess of refluxing 1,2-dibromoethane afforded 63.7% of triphenyltin bromide [based on unrecovered (I)] and no evidence for other tin bromides. Refluxing sym-tetrachloroethane reacted with (I) to give a 55% yield of triphenyltin chloride along with a small amount of tetraphenyltin and an unidentified, probably polymeric, material.

The tetrakis compound is also susceptible to nucleophilic cleavage, and with triphenyltinlithium attack can occur at the lateral position. When the reaction was run in a 4:1 molar ratio, 44% of (I) was recovered unchanged. The only other product isolated was hexaphenylditin. The latter product can arise from hydrolysis of triphenyl-tinlithium⁹ as well as from reaction with the tetrakis compound. The yield of hexaphenylditin based upon unrecovered starting material and the total amount of triphenyltinlithium employed was 74%. It should be noted that in the present reaction attack at the central tin atom should lead to no net reaction, so that all that can be seen is attack at the lateral position.

The reactions above offer reasonably good evidence that the structural assignment is correct. Attention was next centered upon the possibility of cleaving only one tin-tin bond in the tetrakis compound with the hope of obtaining a functionally substituted tris(triphenylstannyl)tin compound. Attempts to accomplish this limited cleavage have as yet been unsuccessful.

Reaction of (I) with one mole of iodine afforded an 81.9% yield of triphenyltin iodide; however, the only other product isolated was unreacted tetrakis compound in a 57\% yield. When (I) was treated with one mole of sym-tetrachloroethane in refluxing xylene, no reaction was observed, and (I) was recovered in 94.2% yield. In like manner the nucleophilic reagent, methyllithium, gave only tetraphenyltin in addition to unreacted starting material.

The conclusion that is drawn from these reactions is that the primary cleavage products formed are more reactive than the tetrakis compound itself. This is perhaps not surprising when one considers the steric hindrance to attack that must be present in the highly branched structure. One might look upon the molecule as containing a sphere of phenyl groups surrounding the vulnerable tin-tin bonds. Investigations of the chemistry of the related compound, tetrakis(trimethylsilyl)silane, have indicated that the same effect is probably operating in that compound also¹⁰. Controlled cleavage with halogens has not been successful; however, organo- and silyllithium compounds do cleave one silicon-silicon bond to produce tris(trimethylsilyl)silane upon hydrolysis. It is not surprising that the reaction of (I) with methyllithium is more complex than the corresponding reaction of tetrakis(trimethylsilyl)silane. The tinlithium species, $(C_6H_5)_2SnLi_2$, has recently been shown¹¹ to be stable in tetrahydrofuran solution, while the analogous silyllithium compound has not been characterized.

An alternate method for forming derivatives of the tris(triphenylstannyl)tin structure was apparently available through reactions of tris(triphenylstannyl)tinlithium, (IV), the intermediate presumed to be present in the preparation of (I) starting from triphenyltinlithium and stannous chloride. The tinlithium intermediate need not necessarily be present in the preparation to account for the formation of the tetrakis compound, since the product could arise from a disproportionation reaction. Indeed, perhaps the most important method for the formation of hexaorganodilead compounds is the reaction of lead dihalides with organometallic compounds¹². In order to test for the presence of (IV), chlorotriphenylgermane was substituted for triphenyltin chloride in the last step of the reaction. A product was obtained with a melting point and solubility properties quite similar to those of (I).

$$3 (C_6H_5)_3 SnLi + SnCl_2 \longrightarrow (IV) \xrightarrow{(C_6H_5)_3GeCl} [(C_6H_5)_3Sn]_3SnGe(C_6H_5)_3$$
(V)

However, the infrared spectrum of the material showed the presence of germaniumphenyl absorptions, and the X-ray powder pattern was distinctly different from that of (I). A molecular weight determination was quite satisfactory for the structure, tris(triphenylstannyl)(triphenylgermyl)tin, (V), but a combined analysis for germanium and tin was low. It might be mentioned that it is difficult to determine the purity of the samples of materials that melt with decomposition over a range of temperature, so that impurities may be the cause of the poor analysis in the case of the latter compound. It is believed that the product is the germanium derivative, (V).

Reactions of (IV) with trimethyl phosphate or methyl iodide gave in low yield a product which is probably methyltris(triphenylstannyl)tin. However, the compound appeared to be relatively unstable in solution and could not be sufficiently purified to obtain an identification.

In contrast to the cases above, reaction of the supposed tris(triphenylstannyl)tinlithium with chlorotriphenylsilane or tri-*n*-butyltin chloride afforded only (I). In like manner, hydrolysis with saturated aqueous ammonium chloride gave the tetrakis compound, but in lower yield than was obtained after derivatization with triphenyltin chloride. The desired product from the latter reaction was tris(triphenylstannyl)tin hydride. The related compounds, tris(triphenylsilane¹³, tris(triphenylgermyl)silane¹⁴ and tris(triphenylgermyl)germane⁴, are known and are quite stable, but the more polar Sn-H bond may cause the tin hydride to be unstable.

It is believed that tris(triphenylstannyl)tinlithium is formed on reaction of triphenyltinlithium with stannous chloride, but there are limits to the synthetic possibilities of the reagent, at least under the conditions employed in the present studies.

ENPERIMENTAL

Triphenyltinlithium in tetrahydrofuran (THF) was prepared according to a published procedure⁹. The THF was dried by refluxing over sodium wire, distillation into lithium aluminum hydride, and distillation from the hydride immediately before use. Melting points were determined with a Mel-Temp apparatus.

Proparation of tetrakis(triphenylstannyl)tin (I)

From triphenyltinlithium and stannous chloride followed by triphenyltin chloride. A solution of 3.66 g (0.019 mole) of stannous chloride in 100 ml of tetrahydrofuran (THF) was cooled to ca. 0° with an ice-water bath, and 118 ml of 0.479 M triphenyltinlithium (0.057 mole) was added over a period of 3 h. The reaction mixture became yellow rapidly, then darkened to brown. At the end of the addition the mixture was stirred for 18 h. The solution appeared homogeneous and gave a negative Color Test I^{13} . It was decanted and added dropwise to a solution of 7.05 g (0.019 mole) of triphenyltin chloride in 100 ml of THF. The resulting brown solution was stirred for 20 h, then hydrolyzed in saturated aqueous ammonium chloride. The organic layer was separated and filtered to obtain a white solid, m.p. 310-330° decomp. Recrystallization from benzene gave 15.7 g (55%) of (I), m.p. 315-330° with some decomposition beginning at about 280°. Subsequent recrystallizations from benzene, chloroform or a carbon disulfide-acetone mixture did not change the melting point characteristics. The infrared spectrum of the compound is identical to that of hexaphenylditin, while the ultraviolet spectrum (λ_{max} in cyclohexane 275.5, 247 m μ) is distinctly different from that of the ditin. (Found: C, 57.71, 57.91; H, 4.14, 4.16; Sn, 38.93, 39.21; mol. wt. vapor pressure osmometer, 1498. C₇₂H₆₀Sn₅ calcd.: C, 56.94; H, 3.98; Sn, 39.08°₀; mol. wt., 1519.)

Evaporation of the THF filtrate afforded a solid which was crystallized from benzene-petroleum ether (b.p. $60-70^{\circ}$) to obtain 4.6 g (17.5%) of hexaphenylditin, m.p. 229-232° (mixed m.p. 230-234°). Concentration of the mother liquor gave a material, m.p. 280-300° decomp., which appeared to be a mixture of the two products already described. The mixture was not fractionated.

A subsequent run of the reaction under the same conditions afforded (I) in a yield of 69.4 %.

From phenylmagnesium bromide and stannous chloride. The Grignard reagent prepared from 75.0 g (0.48 mole) of bromobenzene and 12.2 g (0.50 g-atom) of magnesium in 400 ml of ether was decanted through a glass wool plug into a reaction flask and cooled to ca. 0° with an ice-water bath. Finely powdered stannous chloride, 15.0 g (0.079 mole), was added, and the solution turned red in color as the stannous chloride slowly dissolved. The mixture was allowed to warm to room temperature and stirred for I h, then heated to reflux temperature and stirred for 4.5 h. Hydrolysis was effected in cold water. Filtration of the organic layer gave a brown solid which was triturated with benzene to obtain an insoluble brown solid which did not melt below 400° and 2.7 g of benzene-soluble hexaphenylditin, m.p. 225-230° (mixed m.p. 226-231°). From the original ether layer there was obtained a solid which was fractionally crystallized from benzene to give 3.5 g of additional hexaphenylditin (total yield, 22%) and 0.5 g (2.1% based on stannous chloride) of (I), m.p. 310-330° decomp. (mixed m.p.). The ultraviolet spectrum and X-ray powder diffraction pattern of this compound were identical with those of the previously prepared (I).

From phenyllithium and stannous chloride (attempted). An ether solution (420 ml) of 0.41 mole of phenyllithium was cooled to ca. 0° in an ice-water bath, and 13.0 g (0.068 mole) of stannous chloride was added. The reaction mixture became gray in color within a few min. It was allowed to warm to room temperature and stirred for 1 h, followed by 4 h at reflux temperature. Hydrolysis in saturated ammonium chloride was followed by the usual work-up. The only product obtained was tetraphenyltin, 13.7 g (47.3 % based on stannous chloride), m.p. 228-231° (mixed m.p.).

From triphenyltinlithium and stannic chloride. Triphenyltinlithium was prepared from phenyllithium (0.30 mole in 330 ml of ether) and stannous chloride, 19.0 g (0.10 mole) in 150 ml of ether. The solution was added dropwise to 6.5 g (0.025 mole) of stannic chloride in 100 ml of ether. The resulting mixture was stirred overnight, then hydrolyzed in saturated ammonium chloride. Work-up in the usual manner gave a brown solid which did not melt below 400°; 3.25 g of tetraphenyltin, m.p. $225-227^{\circ}$ (mixed m.p.); 3.9 g (9.7°_{0}) of (I), m.p. $305-325^{\circ}$ decomp.; and additional material melting at 220-230° which was not fractionated. The tetrakis(triphenylstannyl)tin was identical with previous samples in ultraviolet spectrum and X-ray diffraction pattern.

From triphenyltin chloride, stannic chloride and lithium. Solutions of 23.1 g (0.060 mole) of triphenyltin chloride in 300 ml of tetrahydrofuran (THF) and 3.91 g (0.015 mole) of stannic chloride in 30 ml of benzene were added simultaneously over a period of 1.5 h to 0.83 g (0.12 g-atom) of finely cut lithium wire in 100 ml of THF. After approximately half of the addition had been completed, the lithium became shiny, and heat was evolved. The mixture turned pale green in color and was stirred overnight, followed by hydrolysis in saturated ammonium chloride. Work-up in the usual manner gave 8.6 g (41 %) of hexaphenylditin, m.p. 230-234° (mixed m.p. 232-234°), and 4.7 g (20.6%) of (I), identified by m.p. (315-330° decomp.), ultraviolet spectrum and X-ray diffraction pattern.

Reactions of tetrakis(triphenylstannyl)tin (I)

With iodine (1:1 molar ratio). To a solution of 15.18 g (0.01 mole) of (I) in 100 ml of refluxing chloroform was added over a period of 2 h a solution of 2.54 g (0.01 mole) of iodine in 100 ml of chloroform. The iodine color was discharged rapidly throughout the addition, but the reaction mixture developed a yellow color. The solution was cooled and the solvent evaporated. Fractional crystallization of the solid product from benzene-petroleum ether (b.p. 60-70°) gave 7.4 g (49%) of recovered (I), identified by m.p. and ultraviolet spectrum, and 3.9 g (82%) of light yellow triphenyltin iodide, m.p. 118-121° (mixed m.p.). It is believed that the yellow color of the reaction mixture and the solid product was due to the presence of small quantities of stannic iodide, a red-orange solid in the pure state. None of this product was isolated, however.

With iodine (1:4 molar ratio). The previous reaction was repeated employing a solution of 10.16 g (0.04 mole) of iodine in 300 ml of chloroform. The addition was carried out over a period of 4 h. The mixture was allowed to stand for 20 h, followed by evaporation of the solvent. Crystallization of the solid product from petroleum ether (b.p. $28-38^{\circ}$) gave 15.7 g (82.4%) of triphenyltin iodide, m.p. $119-122^{\circ}$ (mixed m.p.). Evaporation of the mother liquor afforded a red-orange material which could not be further purified by crystallization. The material is believed to consist of a mixture of stannic iodide with some additional triphenyltin iodide.

With excess sym-tetrachloroethane. A mixture of 15.18 g (0.01 mole) of (I) and 50 ml of sym-tetrachloroethane was heated to 140° by means of an oil bath and stirred for 18 h. The reaction mixture was heterogeneous throughout this treatment. The mixture was filtered through a sintered glass funnel to obtain a brown solid which was insoluble in boiling benzene and did not melt below 400°. The solvent was distilled from the filtrate and the residue fractionally crystallized from benzene-petroleum ether (b.p. 60-70°) to obtain 0.6 g of tetraphenyltin, m.p. 225-229° (mixed m.p.), and impure triphenyltin chloride. The latter was recrystallized from dry petroleum ether (b.p. 60-70°) to afford 8.5 g (55%) of triphenyltin chloride, m.p. 101-104° (mixed m.p. 102-105°).

With sym-tetrachloroethane (I:I molar ratio, attempted). A mixture of 15.18 g (0.01 mole) of (I) and 1.68 g (0.01 mole) of sym-tetrachloroethane in 100 ml of xylene was heated at gentle reflux for 48 h. The heterogeneous reaction mixture was allowed

to cool. Filtration afforded 13.9 g (91.6 %) of (I), m.p. $315-330^{\circ}$ decomp. (mixed m.p.). Distillation of the solvent followed by crystallization of the residue from benzene-petroleum ether (b.p. 60-70°) gave an additional 0.4 g (2.6%) of (I), m.p. $310-325^{\circ}$ decomp. (mixed m.p.).

The reaction was repeated using only 15 ml of xylene solvent and refluxing for 4S h. Again (I) was recovered in 94 % yield.

With excess 1,2-dibromoethane. A mixture of 15.18 g (0.01 mole) of (I) and 50 ml of freshly distilled 1,2-dibromoethane was stirred for 16 h at 130°. The mixture did not become homogeneous and slowly turned brown. The reaction mixture was cooled and filtered to obtain brown solid which was crystallized twice from benzene-petroleum ether (b.p. 60-70°) to obtain 1.0 g (6.8%) of (I), m.p. 305-325° decomp. (mixed m.p.). 1,2-Dibromoethane was distilled from the filtrate and the resulting solid crystallized twice from dry benzene to obtain 10.2 g [63-7% based on unrecovered (I)] of triphenyltin bromide, m.p. 117-119° (mixed m.p.).

With triphenyltinlihium (1:4 molar ratio). To a solution of 15.18 g (0.01 mole) of (I) in 100 ml of tetrahydrofuran was added dropwise 77 ml of 0.520 M triphenyltinlihium (0.04 mole). During the addition the reaction mixture turned yellow, then brown. After stirring for 48 h, hydrolysis was effected with saturated ammonium chloride. Work-up in the usual manner gave 6.7 g (44%) of recovered (I), m.p. $310-325^{\circ}$ (mixed m.p.), and 16.2 g (74% based on the total amount of triphenyltinlithium plus unrecovered starting material) of hexaphenylditin, m.p. $230-234^{\circ}$ (mixed m.p.).

With methyllithium (1:1 molar ratio). To a solution of 15.18 g (0.01 mole) of (I) in 100 ml of tetrahydrofuran was added 13 ml of a 0.760 M ether solution of methyllithium (0.01 mole). The reaction mixture became light yellow in color, and Color Test I¹⁵ was negative after 45 min of stirring. Hydrolysis in saturated ammonium chloride followed by the normal work-up afforded 8.4 g (55%) of (I), m.p. 310-325° (mixed m.p.), and 0.8 g of tetraphenyltin, m.p. 222-226° (mixed m.p. 224-226°). Additional solid, m.p. 190-200°, which appeared to be a mixture of tetraphenyltin and hexaphenylditin, was obtained but not fractionated.

Reactions of tris(triphenvlstannyl)tinlithium (IV)

With trimethyl phosphate. A solution of (IV), prepared from 104 ml of 0.520 M triphenyltinlithium (0.054 mole) and 3.41 g (0.018 mole) of stannous chloride in 100 ml of tetrahydrofuran (THF), was added dropwise to 2.52 g (0.018 mole) of trimethyl phosphate in 100 ml of THF. The brown reaction mixture was stirred for 24 h, then hydrolyzed in saturated ammonium chloride. Work-up of the organic layer in the usual manner afforded a white solid which was fractionally crystallized from benzene to obtain 8.3 g (39.5%) of hexaphenylditin, m.p. 230-234° (mixed m.p. 232-235°), and solid melting in the range, 165-180°. Recrystallization of the latter material from chloroform gave 3.2 g [15% as methyltris(triphenylstannyl)tin] of white solid, m.p. 180-183°. Three recrystallizations from benzene-petroleum ether [b.p. 60-70°] did not change the melting point. It was noted that a brown sediment began to be deposited from solutions of this material on standing for several hours. (Found: Sn, 39.59, 38.77; mol. wt. vapor pressure osmometer, 944. $C_{55}H_{43}Sn_4$ calcd.: Sn, 40.11%; mol. wt., 1184.)

A second run of the reaction was made, and a similar material was isolated.

Recrystallization from ethyl acetate-methanol raised the m.p. to 183-185°. A mixture melting point with the solid from the first run was not depressed. A molecular weight determination (vapor pressure osmometer) gave a value of 1002 (calcd. 1184). It seems likely that the product is the desired methyltris[triphenylstannyl]tin, but a pure sample has not yet been obtained.

With methyl iodide. A reaction exactly analogous to that above was run, except that derivatization was carried with methyl iodide instead of trimethyl phosphate. Hexaphenylditin (32.7%) was obtained along with 4.8% of the same product as above, m.p. 181-184% (mixed m.p.). Again further purification of the latter product could not be effected.

With chlorotriphenylgermane. A solution of 0.017 mole of (IV) was added dropwise to 5.76 g (0.017 mole) of chlorotriphenylgermane in 100 ml of tetrahydrofuran. The reaction mixture was stirred for 45 h, then hydrolyzed in saturated ammonium chloride. Separation and filtration of the organic layer gave white solid, m.p. 315-330° decomp. This material was recrystallized twice from benzene-petroleum ether (b.p. $60-70^{-2}$) to give 4.4 g (18%) of the product with the same melting point. The m.p. was not depressed when mixed with (I); however, an infrared spectrum of the product (carbon disulfide) showed an absorption at 9.24 μ characteristic of the germaniumphenyl linkage in addition to the tin-phenyl absorption at 9.36 μ . The X-ray powder diffraction pattern of the product was distinctly different from that of (I) and did not appear to be the pattern to be expected for a mixture of (I) with another product containing germanium-phenyl linkages. The product is probably tris(triphenylstannyl)(triphenylgermyl)tin. (Found: Ge + Sn, 35.58, 35.99; mol. wt. vapor pressure osmometer, 1503. $C_{72}H_{60}$ GeSn₄ calcd.: Ge + Sn, 37.17%; mol. wt., 1473.)

With chlorotriphenylsilane. A solution of 0.019 mole of (IV) was added to 5.60 g (0.019 mole) of chlorotriphenylsilane in 75 ml of tetrahydrofuran. The reaction mixture was stirred overnight, then hydrolyzed in saturated ammonium chloride. Work-up in the normal manner gave 13.0 g (57 %) of (I), m.p. 315–330% (mixed m.p.). The infrared spectrum of the product showed no evidence of silicon-phenyl absorptions, and the ultraviolet spectrum was identical to that of previously prepared (I).

With tri-n-butyltin chloride. Tris(triphenylstannyl)tinlithium (IV) (0.019 mole) was prepared as described above and added to 6.18 g (0.019 mole) of tri-n-butyltin chloride in 75 ml of tetrahydrofuran. The mixture was stirred overnight, then worked up in the normal manner. The only product obtained was (I), 15.3 g (67.2 %), which was identified by mixture melting point, infrared and ultraviolet spectra.

With saturated aqueous ammonium chloride. A solution of 0.019 mole of (IV) was hydrolyzed by pouring into saturated ammonium chloride. Work-up as before gave 7.6 g (34.1%) of (I), identified by mixture melting point, ultraviolet spectrum and X-ray powder pattern. In addition, 3.1 g (14.5%) of hexaphenylditin, m.p. 230-234% (mixed m.p. 232-235%), was obtained from the work-up of the organic layer.

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SUMMARY

Methods for the preparation of tetrakis(triphenylstannyl)tin (I), the first branched-chain polytin compound in the literature, are described. Detailed evidence for the structure of the compound is presented. The compound reacts with both electrophilic and nucleophilic reagents with tin-tin bond cleavage; however, controlled cleavage of a single Sn-Sn bond in the tetrakis structure has not yet been achieved. The reactive intermediate, tris(triphenvlstannyl)tinlithium, has been characterized through treatment with chlorotriphenvlgermane to form tris(triphenvlstannvl)-(triphenylgermyl)tin.

REFERENCES

- I H. GILMAN AND F. K. CARTLEDGE, Chem. Ind. (London), (1964) 1231.
- 2 H. GILMAN AND C. L. SMITH, J. Am. Chem. Soc., 86 (1964) 1454.
- 3 J. BÖESEKEN AND J. J. RUTGERS, Rec. Trav. Chim., 42 (1923) 1017. 4 F. GLOCKLING AND K. A. HOOTON, J. Chem. Soc., (1963) 1849. 5 D. N. HAGUE AND R. H. PRINCE, Proc. Chem. Soc., (1962) 300.

- 6 W. DRENTH, M. J. JANSSEN, G. J. M. VAN DER KERK AND J. A. VLIEGENTHART, J. Organometal. Chem., 2 (1964) 265.
- 7 L. C. WILLEMSENS AND G. J. M. VAN DER KERK, J. Organometal. Chem., 2 (1964) 260, 271.
- S J. J. GOODMAN, unpublished Ph.D. thesis, Iowa State University, Ames, Iowa (1955).
 H. GILMAN, O. L. MARRS AND S.-Y. SIM, J. Org. Chem., 27 (1962) 4232.
 IO H. GILMAN AND C. L. SMITH, unpublished studies.

- IT H. SCHUMANN, K. F. THOM AND M. SCHMIDT, J. Organometal. Chem., 2 (1964) 97.
- 12 H. GILMAN AND J. C. BAILIE, J. Am. Chem. Soc., 61 (1939) 731; G. BÄHR AND G. ZOCHE, Chem. Ber., 85 (1955) 542.
- 13 D. WILTENBERG, M. V. GEORGE AND H. GILMAN, J. Am. Chem. Soc., S1 (1959) 4812.
- 14 J. G. MILLIGAN AND C. A. KRAUS, J. Am. Chem. Soc., 72 (1950) 5297-
- 15 H. GILMAN AND F. SCHULZE, J. Am. Chem. Soc., 47 (1925) 2002.

[. Organometal. Chem., 5 (1966) 48-56